

vdW-DF study of energetic, structural, and vibrational properties of small water clusters and ice I_h

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We present results for a density functional theory study of small water clusters and hexagonal ice I_h , using the van der Waals density functional (vdW-DF). In particular, we examine energetic, structural, and vibrational properties of these systems. Our results exhibit excellent agreement with both experiment and quantum-chemistry calculations and show a systematic and consistent improvement over standard exchange-correlation functionals—making vdW-DF a promising candidate for resolving longstanding difficulties with density functional theory in describing water. In addition, by comparing our vdW-DF results with quantum-chemistry calculations and other standard exchange-correlation functionals, we shed light on the question of why standard functionals often fail to describe these systems accurately.

I. INTRODUCTION

Despite the overwhelming abundance of water on Earth's surface and its composing the majority of all known life, much of the physics of water remains a mystery. Unraveling that mystery requires the ability to take microscopic information and extend it toward the macroscopic regime. Classical force fields and other parameterized models can calculate average macroscopic properties of water well,^{1–3} but generally yield little insight into the microscopic physics underpinning these properties. On the other hand, quantum-chemistry methods such as Møller-Plesset perturbation theory and coupled-cluster techniques have been invaluable in understanding numerous molecular systems and indeed are responsible for much of what is understood about water today.^{4–7} But, their poor scaling with system size limits their use to systems containing only a few molecules.⁸ Density functional theory (DFT) scales substantially better and is thus, in principle, well suited to make the connection to the macroscopic regime. Unfortunately, standard functionals fail to adequately describe the weak van der Waals interactions that are critical to obtain accurate diffusive and structural properties of water.^{9–13}

Many of water's interesting properties stem from its ability to form complex hydrogen-bonded structures, the description of which requires an accurate treatment of dispersion interactions. Historically, DFT has done a poor job of treating these weak interactions. Recent interest in van der Waals systems has led to the development of a number of successful approaches aimed at improving DFT's ability to incorporate dispersion interactions accurately. These include post-processing^{14,15} and semi-empirical methods^{16,17} as well as hybrid^{18,19} and non-local functionals.^{20,21} Here, we focus on the recently developed van der Waals density functional (vdW-DF), a truly non-local functional which fits seamlessly into DFT. This functional has been successfully applied to a variety of other weakly binding systems,^{22–28} and is known to hold promise for improving DFT's description of the hydrogen bonding in water.^{29–34} Here, we use it to perform

systematic calculations on small water clusters $(\text{H}_2\text{O})_n$ with $n = 1–5$ and standard ice I_h . Comparison with experiment and second-order Møller-Plesset perturbation theory (MP2) calculations demonstrates that DFT, utilizing vdW-DF, is able to obtain excellent results for a wide variety of water's properties, even in large, bulk-like systems.

II. COMPUTATIONAL DETAILS

Our DFT calculations were carried out using the plane-wave self-consistent field (PWSCF) code within the QUANTUM-ESPRESSO package,³⁵ utilizing ultrasoft pseudopotentials. For comparison, in addition to vdW-DF we used a standard local functional (LDA) and a semi-local functional (PBE). The three functionals all used Slater exchange and Perdew-Wang correlation³⁶ to describe local exchange and correlation. For the PBE functional, the gradient correction approach of Perdew, Burke, and Ernzerhof was used.³⁷ For vdW-DF, semi-local exchange was provided by a revised PBE scheme³⁸ and non-local correlation was provided by vdW-DF.^{20,21} Wavefunction and charge-density cutoffs were 35 Ry and 420 Ry, respectively. A self-consistency convergence criterion of at least 1×10^{-10} Ry was used for all water cluster calculations and 1×10^{-8} Ry for ice I_h . Initial structures were relaxed until all force components were less than 1×10^{-5} Ry/a.u. in the water clusters and 1×10^{-4} Ry/a.u. for ice. Stress relaxations were carried out in all ice calculations by relaxing each free lattice parameter until all stress components were smaller than 1 kbar. To minimize interactions between periodic images, simulation cells for the finite systems were sized to ensure a minimum separation of 10 Å between atoms in one cell and atoms in neighboring cells.

MP2 calculations were carried out using the quantum-chemistry package GAUSSIAN,³⁹ employing Dunning's augmented, triple-zeta basis set (aug-cc-pVTZ). It has been shown that this basis set is sufficient to yield accurate properties for small water clusters,⁴ and simple testing with the larger aug-cc-pVQZ basis set confirmed

only minimal changes in the properties of interest here. Additionally, the MP2 binding energies obtained here are within 5% of those reported by Santra et al.⁴⁰ who extrapolated to the complete basis set. While counterpoise corrections were deemed negligible for most properties of interest, we found that they alter the vibrational frequencies by as much as 6% in the water dimer. For this reason, counterpoise corrections were applied to all MP2 calculations carried out in this work. Initial water cluster structures were relaxed until all forces were less than 4×10^{-6} Ry/a.u. Detailed positions for all optimized structures are provided in the supplementary materials.

Vibrational frequencies for the MP2 method were calculated directly, using GAUSSIAN. For the DFT calculations, forces on all atoms were calculated when each atom was displaced by ± 0.0025 , ± 0.005 , ± 0.0075 , and ± 0.01 Å along each of the three Cartesian directions. The dynamical matrix was then built by taking the first derivative of the forces using a nine-point numerical derivative. All systems stayed within the harmonic regime for all displacements employed.

III. RESULTS

A. Binding, Structure, and Electric Dipole Moment

We start by presenting results for the binding energies of the water clusters $(\text{H}_2\text{O})_n$ with $n = 2 - 5$, and standard, hexagonal ice I_h . The results are shown in Fig. 1(a), along with MP2 values for the water clusters and the experimental value for ice I_h .⁴¹ Also shown for reference are values from two of the most popular local (LDA) and semi-local (PBE) functionals in use today. As can be seen in the figure, the LDA and PBE functionals exhibit a distinct overbinding. This is also evident in Fig. 1(b), which shows the average oxygen-oxygen distance compared with experiment for both the clusters⁴² and ice I_h .⁴³ The vdW-DF values are in excellent agreement with experiment and show a clear improvement over LDA and PBE, which draw the oxygen atoms too close together, consistent with the overbinding seen in Fig. 1(a).

Interestingly, a recent study by Wang et al.³³ has pointed out that, despite showing a substantial improvement over other functionals when calculating the self-diffusion and density of liquid water, vdW-DF tends to understructure the liquid. This understructuring manifests itself as a lowered density in the second coordination shell of the oxygen-oxygen radial distribution function. Wang et al. point out that this understructuring is likely an artifact of the chosen semi-local piece of the exchange functional, rather than a problem within the non-local correlation functional of vdW-DF. Many groups are investigating the effects of different exchange functionals on vdW-DF and it will be interesting to see if the understructuring problem can be solved.

Another important quantity is the bulk modulus—a

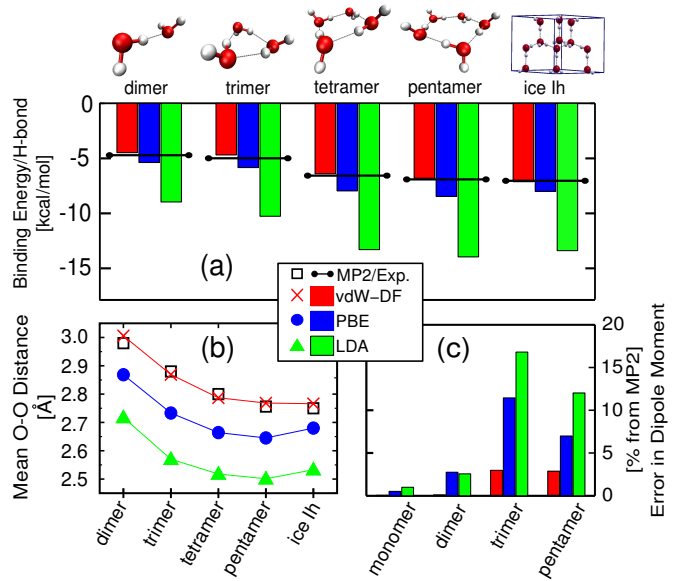


FIG. 1. (a) Binding energy per hydrogen bond for each of the multimers and ice I_h . The horizontal black lines correspond to MP2 calculations for the clusters and experiment for ice.⁴¹ (b) Average oxygen-oxygen distance in each system. The black boxes represent experimental values.^{42,43} (c) Percent error relative to MP2 calculations of the dipole moment. The dipole moment of the tetramer is not shown since it is zero by the S_4 symmetry of the complex.

property that depends on the curvature of the energy surface when the system is subjected to isotropic expansion or contraction. In a recent study,²⁹ vdW-DF was used to calculate the bulk modulus of ice I_h . This study found vdW-DF to be in good agreement with the experimental value and serves as an independent extension of the findings presented here.

To probe the accuracy of the electronic structure itself, the dipole moments were calculated for the finite systems. Figure 1(c) shows the errors obtained (relative to MP2 calculations) for the three functionals studied here. Experimental results could not be found for clusters larger than $n = 2$,⁴⁴ but MP2 results agree with available experimental results to within 1%, so MP2 is used as the reference throughout Fig. 1(c). Detailed values for all dipole moments are presented in the supplementary materials. Again, results obtained from vdW-DF are in excellent agreement with these high-level quantum-chemistry calculations, while LDA and PBE show substantial errors.

One can understand the better performance of vdW-DF since it is a non-local functional, but the physical ramifications of this distinction can be seen in Fig. 2. The figure shows the calculated charge density along a line from oxygen to hydrogen through both the covalent bond (solid lines) and the hydrogen bond (dashed lines). Not surprising, the charge densities corresponding to the covalent bond for each functional are nearly indistinguishable. However, when looking at the curves cor-

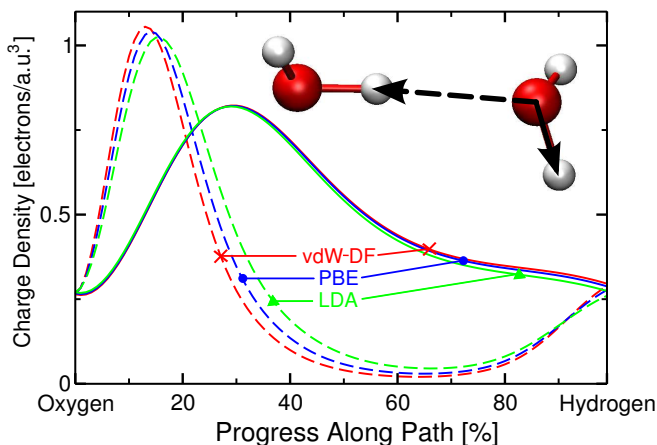


FIG. 2. Calculated valence charge density for the water dimer along the lines between the indicated oxygen and hydrogens through both the covalent bond (solid lines) and the hydrogen bond (dashed lines) for the three different functionals.

responding to the charge density in the hydrogen bond, the cause for the overbinding of LDA and PBE—evident throughout Fig. 1—is revealed. Both PBE, and to an even greater extent LDA, shift the peak of charge density from the oxygen toward the hydrogen, resulting in an increase in the covalent character of the bond. (Note that, in the critical region between 20% and 60% along the path, LDA overestimates the charge density by as much as a factor of 2.) This, in turn, strengthens the bond and creates an overbinding that permeates all results calculated with these functionals.

B. Vibrational Frequencies

Sit and Marzari¹³ calculated the vibrational frequencies of the water dimer using the PBE functional. They found that PBE performed reasonably well, but significant discrepancies from experiment were found for some modes, particularly low-frequency, inter-molecular modes. They postulated, as have others,³² that the problem arose at least in part from the inability of local and semi-local functionals to correctly treat the hydrogen bond. To extend this investigation, we performed similar frequency calculations for all the water clusters—monomer through pentamer—using all three functionals and MP2. (Our results for the dimer using PBE are very similar to those of Sit and Marzari.) The results for the larger water clusters exhibit trends similar to those found in the dimer. Figure 3 shows our DFT-calculated and available experimentally-determined vibrational frequencies for the monomer,⁴⁵ dimer,⁴⁵ and trimer;⁴⁶ reliable experimental results for larger clusters could not be found. Results for all clusters compared with MP2 and the frequencies of ice I_h calculated with the three functionals are collected in the supplementary materials. It should

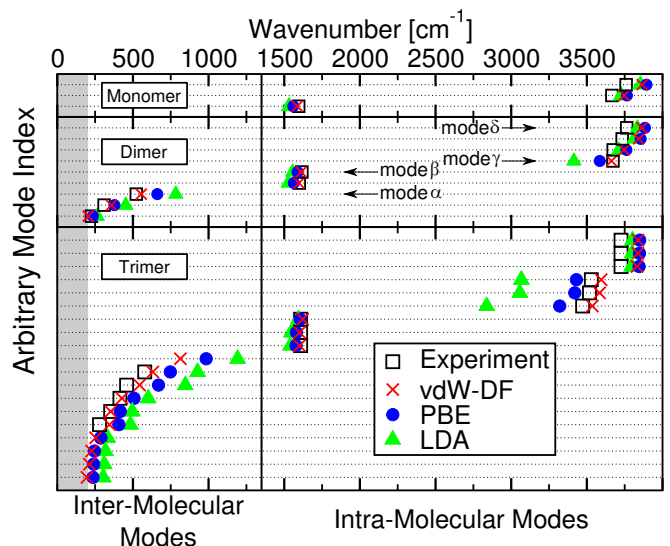


FIG. 3. Vibrational frequencies calculated with the LDA, PBE, and vdW-DF functionals compared to experimental values for the water monomer,⁴⁵ dimer,⁴⁵ and trimer.⁴⁶ The vertical line denotes a separation between inter-molecular dominated and intra-molecular dominated modes. The region between 0 cm^{-1} and 200 cm^{-1} (shaded area) was not included in the analysis. A detailed analysis of the dimer modes labeled mode α , β , γ , and δ is given in Figs. 4 and 5. A full tabulation of mode frequencies for all methods can be found in the supplementary material.

be noted that the frequencies calculated in this work were obtained using the harmonic approximation and no corrections were made for anharmonic effects. Such effects are known to be present in experimental results and can be influential in setting the precise frequency of various oscillations. Calculations including such effects have recently been reported at the PBE and PBE0 level,⁴⁷ but a direct comparison is not possible since the frequencies reported are for the deuterated monomer and dimer. Typically, the changes induced by anharmonic effects are on the order of a few percent and fair comparisons can still be made to experiment. Nevertheless, in this work, truly quantitative comparisons of DFT results were done with respect to the harmonic approximation within MP2.

As can be seen in Fig. 3, all DFT methods get similar results for the monomer frequencies—not surprising since this is a system consisting solely of covalent bonds. Significant deviations occur in some modes for the larger clusters, however. These deviations are worse in the low-frequency region where inter-molecular interactions dominate. Most of the intra-molecular-dominated frequencies are obtained satisfactorily with all three functionals, but a few show significant error in LDA and PBE. Even within the intra-molecular modes there are oscillations which substantially change the hydrogen-bond geometry, so a proper treatment of non-local interactions is necessary to obtain quantitatively correct frequencies. Overall,

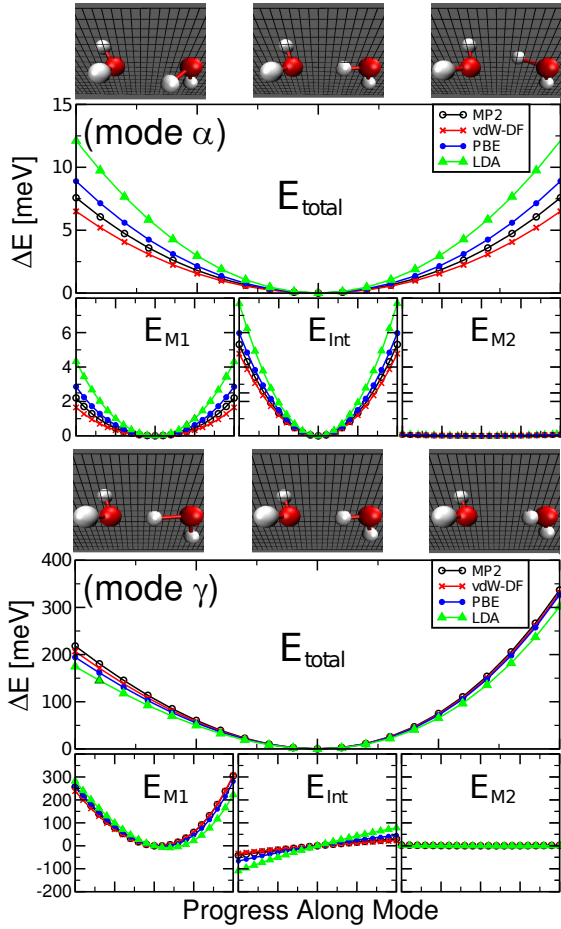


FIG. 4. Energy changes according to Eq. (1) as the water dimer is forced along the normal modes marked α and γ in Fig. 3. The x-axes are on the same scale and represent a dimensionless progress variable along the mode. The insets above show the motion of the water molecules for each particular mode. The grids lie in a plane containing the hydrogen bonding O–H–O in the equilibrium position. In this figure, the hydrogen donor molecule is designated M1 and the hydrogen acceptor molecule is designated M2.

vdW-DF shows a consistent improvement for a majority of the modes. A full tabulation of modes for all methods and systems (including ice I_h) is given in the supplementary materials.

While some modes are well reproduced with all functionals, others show a distinct spread in frequencies for different functionals. This is to be expected for intermolecular modes, but it is somewhat surprising for the intra-molecular modes. This spread is caused largely by the different functionals' varying ability to accurately represent the hydrogen bond, as can be seen by a deeper analysis of some representative modes of the dimer system. Four such modes—labeled mode α , mode β , mode γ , and mode δ —are marked in Fig. 3. Modes α and γ show a large spread in frequency for different functionals, while modes β and δ exhibit much less variation. We

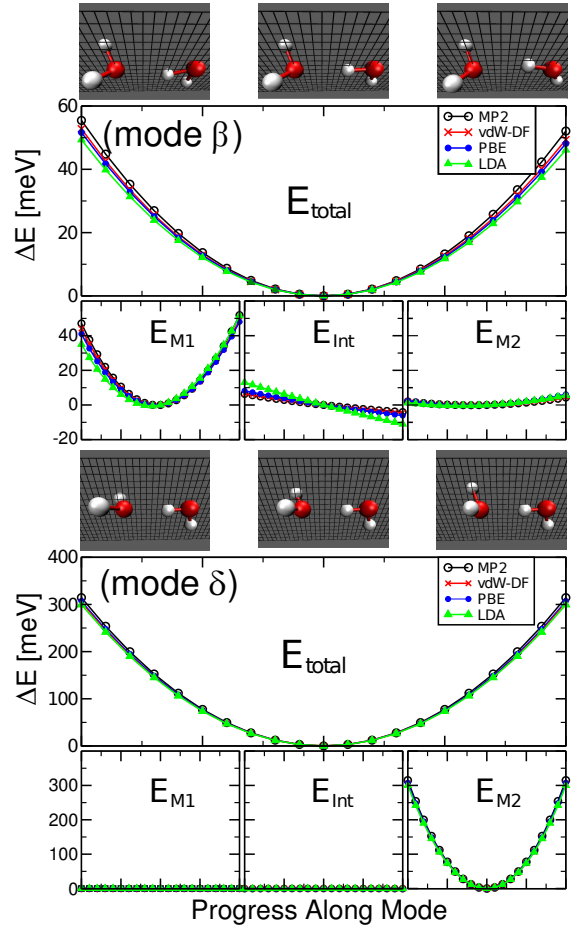


FIG. 5. Same as Fig. 4, except here shown for the modes marked β and δ in Fig. 3.

analyze these modes in greater detail as follows.

The change in energy of any dimer configuration relative to the equilibrium configuration can be written as

$$\Delta E_{\text{total}} = \Delta E_{M1} + \Delta E_{M2} + \Delta E_{\text{int}}, \quad (1)$$

where ΔE_{M1} and ΔE_{M2} are the strain energies within monomers 1 and 2, respectively, and ΔE_{int} is the difference in their interaction energy. As the atoms are moved along a certain mode, the individual contributions in Eq. (1) can increase, decrease, or remain unchanged, depending on whether they enhance, inhibit, or are irrelevant to the change in energy for small excitations of that particular mode. The change in energy coming from these contributions relative to the overall energy change determines how much each energy term contributes to the vibrational frequency.

Figures 4 and 5 show the contributions of the various energy terms in Eq. (1) as the dimer is displaced in both directions along the normal modes α , β , γ , and δ . This was done in step sizes of 0.01 times the (normalized) eigenvectors, to a maximum value of 0.1 times the eigenvectors. Mode α is comprised mainly of an out-of-plane oscillatory motion of the hydrogen donor water molecule.

Oscillations along this mode clearly change the geometry of the hydrogen bond. Since the overall energy change upon movement along this mode is relatively small, the interaction energy makes up a significant portion of the total restoring force. As the different functionals have a varying degree of success in describing the interaction energy, a significant spread in E_{total} and the frequencies results for different functionals. The motion for mode γ consists mainly of a symmetric stretch of the hydrogen donor molecule. Again, this substantially changes the interaction energy as the dimer oscillates along the mode, resulting in a spread in E_{total} and the frequencies. On the other hand, mode β in Fig. 5 is comprised mostly of an angle flex in the hydrogen donor molecule. As with mode α , oscillations along this mode change the hydrogen bond angle and, thus, the interaction energy. Unlike mode α , however, the intra-molecular motions in this mode cause the total energy to change by a relatively large amount. In this case it is enough to swamp the effect from the relatively weak energy change stemming from the changing hydrogen bond geometry. As a result, all functionals find similar frequencies for this mode. Mode δ corresponds to an asymmetric stretch of the hydrogen acceptor molecule. This has virtually no effect on the hydrogen-bond geometry. The frequency of this mode is governed almost entirely by the intra-molecular strain energy in the hydrogen acceptor molecule, with the interaction energy playing virtually no role. Thus, all functionals predict very similar frequencies for this mode. Qualitatively, for the four modes discussed the spread in E_{total} is proportional to the relative spread in frequency in Fig. 3.

To conclude our study of the vibrational properties, the vdW-DF frequencies of all clusters, including the tetramer and the pentamer, were quantitatively compared to MP2 calculations. The results of this analysis are shown in Fig. 6 in the form of histograms of the errors (in percent relative to MP2), analyzing 90 modes in total (as in Fig. 3, modes with a frequency less than 200 cm^{-1} were not included). Again, a complete listing of frequencies for these modes can be found in the supplementary material. In the figure a negative percent error simply means the calculated value was *below* the MP2 value. LDA shows a distinct bimodal distribution in errors. These correspond to a systematic overestimation of the frequency of low-frequency, inter-molecular modes and less pronounced underestimation of the high-frequency, intra-molecular modes relative to MP2. PBE has a much tighter error range but still shows the bimodal distribution evident in the LDA results, and for the same reason. As discussed above, both functionals form an artificially strong hydrogen bond. This—together with the fact that inter-molecular interactions tend to enhance the overall restoring force for inter-molecular modes and to weaken it in intra-molecular modes—results in the bimodal distribution in the LDA and PBE results. The vdW-DF plot shows an error spread that is much less severe and does not exhibit the bimodal distribution char-

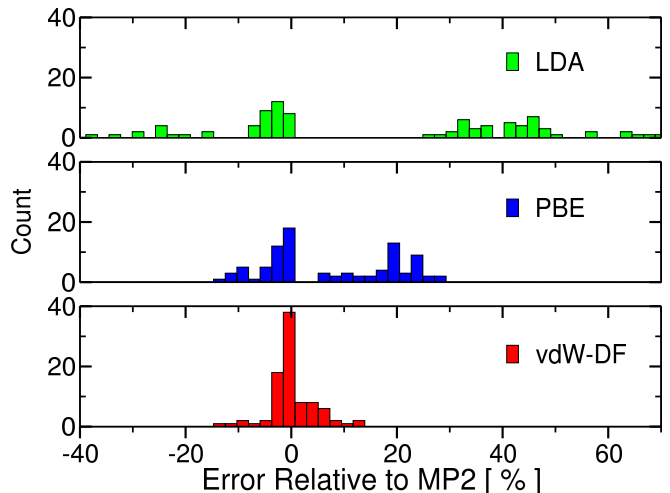


FIG. 6. Histograms of the percent error relative to MP2 calculations over all the frequencies of the clusters. The horizontal axis gives the percent error and the vertical axis gives the number of vibrational frequencies that had that error.

acteristic of systematic hydrogen-bond overestimation. From Figs. 3 and 6 it is clear that vdW-DF systematically improves upon commonly used functionals and demonstrates great promise to accurately reproduce vibrational frequencies of water.

IV. CONCLUSIONS

We have used density functional theory incorporating the van der Waals density functional to calculate a number of properties of small water clusters $(\text{H}_2\text{O})_n$ with $n = 1 - 5$ and hexagonal ice I_h . Our results show excellent agreement, both with experiment and high-level quantum-chemistry calculations. Since DFT is capable of calculating systems with a thousand atoms or more, this implies that accurate quantum-mechanics can now be applied to bulk-like water. This capability should rapidly advance our detailed knowledge and understanding of bulk water behavior.

Toward this aim, the authors, working in collaboration with the developers of the free, open-source QUANTUM-ESPRESSO package,³⁵ have implemented an efficient⁴⁸ vdW-DF functional in the newest official release. We strongly encourage the testing and application of this, and the newer vdW-DF2⁴⁹ functional (also implemented in QUANTUM-ESPRESSO) in water-based systems and, indeed, in any system where hydrogen bonding is expected to play a critical role.

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